

ANOMALOUS X-RAY DIFFRACTION THROUGH CALCITE

by *WEO*

WILLIAM EDWARD O'CONNOR

B. S., St. Benedict's College, 1966

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1969

Approved by:

R. Dean Dargatzis
Major Professor

LD
2688
74
1968
028

TABLE OF CONTENTS

	Page
INTRODUCTION	1
THEORETICAL CALCULATION	8
Formal Theory	9
H·r Method	24
THE EXPERIMENT	29
Determination of Planes in Calcite to Investigate	38
Determination of Angles Between Planes	41
X-Ray Diffraction Techniques	44
Analysis of Data	46
CONCLUSION	52
SUMMARY	55
REFERENCES	57
APPENDIX	59
ACKNOWLEDGMENT	64
VITA	65

INTRODUCTION

In 1941, Borrmann observed anomalously large diffracted and transmitted x-ray beams obtained from propagation through thick single crystals.^{(3)*} This effect has since been named the Borrmann effect and is the first published reference to anomalous transmission.

Ordinarily one would expect x-rays to be absorbed according to the usual expression for absorption: $I = I_0 e^{-\mu_0 t}$. If one were to use a crystal of such a thickness that $\mu_0 t = 10$, then the normally expected incident beam would be attenuated by e^{-10} in passing through the crystal or, in other words, there would be no observable transmitted beam. The fact that there are large transmitted beams would seem to indicate that the normal photoelectric or kinematic effect is not valid in this case. The explanation for this phenomena lies in the dynamical theory of x-ray diffraction.

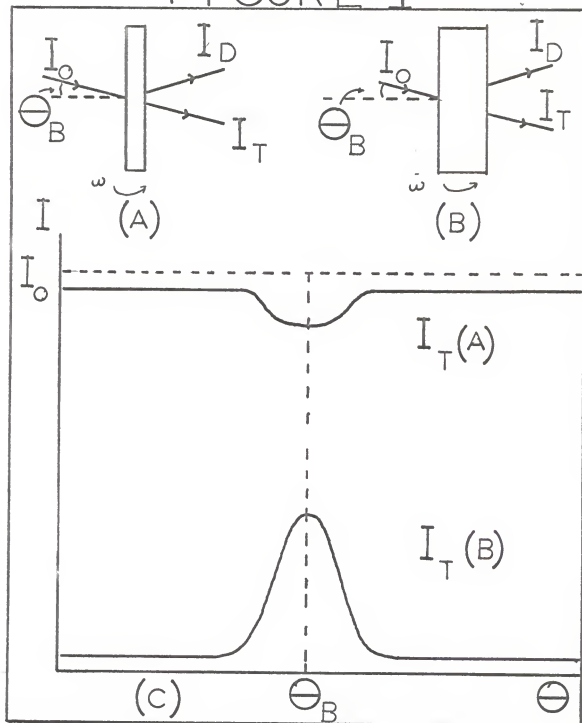
Consider figure 1. A single crystal, cut in the form of a parallel sided slab with the planes to be used in the diffraction perpendicular to the slab faces, is rotated about an axis perpendicular to the plane of the figure. If the crystal is oriented in such a way that the Bragg condition, $\lambda = 2d \sin \theta_B$ is not satisfied, then the intensity is given by $I = I_0 \exp(-\mu t)$. If two crystals are considered, one for which $\mu t \ll 1$ and the other having $\mu t \gg 10$, then a rotation of one of the crystals through θ_B results in the observed phenomena in Part C of the figure. For the thin crystal there is a decrease in transmitted intensity as the crystal reaches the Bragg angle, however, for the thick crystal there is a marked increase in

*References are on page 57

EXPLANATION OF FIGURE 1

Anomalous transmission. (a) Thin crystal Laue diffraction.
(b) Thick crystal Laue diffraction. (c) Transmitted intensity for thin crystal case is shown in upper curve and thick crystal case in lower curve. The peaking of the lower curve at $\theta = \theta_B$ is the anomalous transmission.

FIGURE 1



transmitted intensity. That this effect is due to diffraction is borne out by figure 2.

If the thin crystal in this figure is set for Bragg diffraction and a film is placed behind the crystal, there will appear three small dark areas on the film. Area (1) is due to diffraction; area (2) is approximately equal in intensity to area (1) and at a distance from area (1) corresponding to the proper angle 2θ for diffraction; the third area, directly in line with the incident beam, is very weak. The fact that area (2) is almost as intense as area (1) and that the distance from area (2) to area (3) is proportional to the thickness of the crystal would seem to indicate that the x-rays are channeled down the atomic planes and are attenuated little by the crystal.

The dynamical theory of diffraction explains this phenomenon well, due to the fact that in it diffraction is handled as being a scattering effect of the crystal as a whole, whereas the kinematic theory fails to predict the result because it considers the scattering as being a process associated with individual atoms in the crystal. The dynamical treatment may be considered as looking at the crystal as though the atom planes along the direction of the x-rays were mirrors. At the correct wave length a wave field is established and little or no attenuation takes place. If the crystal is too thin, there are not enough atomic planes to establish this x-ray wave field so a transmitted beam is reduced at the Bragg angle.

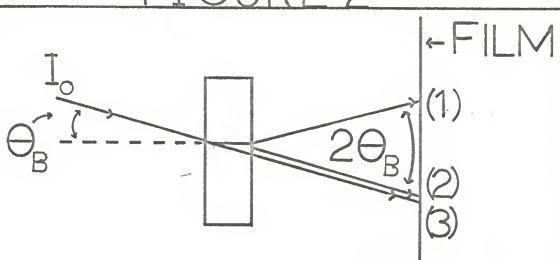
This anomalous transmission does not take place along all directions in the crystal to the same degree. Various parameters have to be taken into consideration to determine the amount of anomalous transmission along a given direction. This amount of transmission is related to a quantity

EXPLANATION OF FIGURE 2

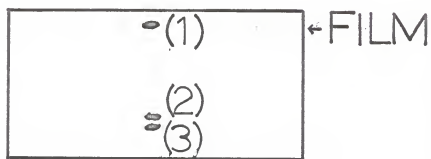
Geometry of the beams when anomalous transmission is occurring.

- (a) Ray diagram required to explain spots on the film. (b) The energy in the diffracted beam (1) and forward diffracted beam (2) apparently flows along the atomic planes in the crystal.

FIGURE 2



(a)



(b)

called epsilon, ϵ , which varies from 0 to 1 depending on the direction of the x-rays in the crystal. The quantity ϵ may be looked at as being a term added to the ordinary absorption such that $I = I_0 \exp [-\mu_r(1-\epsilon)]$. That is, if $\epsilon = 1$, then $I = I_0$, and if $\epsilon = 0$ the standard absorption results.

This quantity epsilon is not only related to the direction in the crystal, but may also be related to temperature effects, i.e., lattice vibration.

B. Okkerse¹¹ has shown that the temperature dependence of the quantity epsilon is $\epsilon = \epsilon_0 \exp(-M)$. Epsilon is a measured value; ϵ_0 is the calculated value related to the distribution of absorbing power in the crystal of the various atoms as obtained from the incoherent scattering factors of the electron; M is the Debye-Waller factor $M = \frac{2\pi^2}{3} \langle u^2 \rangle \frac{\sin^2 \theta}{\lambda^2}$ (u is the root mean square amplitude of vibration).

It is the purpose of this experiment to determine the values of epsilons for several calcite (CaCO_3) planes both theoretically and experimentally and make a comparison between them.

THEORETICAL CALCULATIONS

The theoretical values for epsilon, ϵ_0 , can be calculated in two different ways. Both methods will be discussed here.

The first method of calculating epsilon is based on a calculation made by Boris W. Batterman¹ on germanium.

Nomenclature

$F(hkl)$	$F'(hkl) + \ell F''(hkl)$ Crystal structure factor
P	Polarization factor = 1 or $\cos 2\theta$ for σ and π polarization, respectively
θ_B	Bragg angle
H_{hkl}	Reciprocal lattice vector hkl reflection
f_j, f_j^0	Atomic scattering factor for the j^{th} electron in the atom with and without dispersion, respectively
Z_j	Number of electrons of type j in atom
λ, ω_j	Wave length and angular frequency of absorption edge for j electrons
r_0	Classical electron radius
N	Number of unit cells per unit volume
λ	X-ray wave length
M	Debye Waller factor for amplitude

As was stated in the introduction, the dynamical theory, unlike the kinematic theory, takes into consideration scattering of x-rays by the entire crystal rather than by point sources. Consequently, in the dynamical theory Maxwell's equations are solved for the condition of a complex dielectric constant within the crystal. A resultant equation for the ratio of the diffracted to the incident intensity is derived with some calculation. No attempt will be made to derive this equation. A good explanation of this

derivation may be found in Zachariasen,¹¹ or Batterman and Cole.²

For the case of centrosymmetric crystal, this value for the ratio of the intensities is given by Hirsch⁶ as

$$\frac{I_H}{I_0} = \frac{I_T}{I_0} = \frac{1}{2} \exp(-\mu_0 t_0 / \gamma_0) \cosh 2AK$$

where γ_0 is the cos of the angle of incidence to the normal of the incident surface, μ_0 is the linear absorption coefficient, and

$$2AK = PF''(hkl)/F''(000)$$

From this equation a "new" absorption coefficient can be derived.

It is necessary that an average over the two types of polarization be taken letting

$$\frac{I_H}{I_0} = \frac{1}{2} \exp(-\mu_0 t_0 / \gamma_0)$$

or equating it to

$$\frac{I_H}{I_0} = \frac{1}{2} \exp(-\mu_0 t_0 / \gamma_0) \cosh(2AK)$$

results in

$$\mu_0 = \mu_0 \left[1 - PF''(hkl)/F''(000) \right]$$

epsilon, ϵ , is defined to be the ratio

$$\epsilon = PF''(hkl)/F''(000)$$

where this is the ratio of the imaginary parts of the scattering factor for the hkl and 000 reflections, respectively. Thus, the theoretical value of epsilon can be obtained by finding $F''(hkl)$ and $F''(000)$, respectively.

The structure factor for a crystalline (hkl) reflection is given by the summation over all atoms in the unit cell

$$(1) \quad F_{hkl} = \sum_n f_n \exp(2\pi i \mathbf{r}_n \cdot \mathbf{H}_{hkl})$$

where \mathbf{r}_n is a vector from an origin in the unit cell to the n^{th} atom. All possible values of $\exp(2\pi i \mathbf{r}_n \cdot \mathbf{H}_{hkl})$ are calculated for each atom in the crystal. The position of the atoms is obtained from Wyckoff.¹³

The atomic scattering factor f_m for each atom may be considered to be imaginary, that is

$$f = f^0 + \Delta f' + i \Delta f''$$

where $\Delta f'$ and $\Delta f''$ are the Honl⁷ or dispersion corrections and are dependent on the frequency of the incident radiation, while f^0 is the form factor depending on charge distribution and is independent of frequency. For a particular crystal f^0 , $\Delta f'$, and $\Delta f''$ vary with a change in $\frac{\sin \theta}{\lambda}$; that is, if two planes of diffraction have different d-spacing, the values of f^0 , $\Delta f'$, and $\Delta f''$ are not the same for the two planes. The term $\Delta f'$ is the modification of the atomic scattering when the radiation used is close to the absorption edge of one of the atoms in the sample. Since the wavelengths that were used here are not near the absorption edges for any of the atoms in calcite, $\Delta f'$ is small compared to f^0 and will need no longer be considered. So for the purposes of this work f reduces to

$$f = f^0 + i \Delta f''$$

The value of f^0 is given by

$$f^0 = \sum_j Z_j f_j^0$$

Where Z_j is the number of electrons of a given type in the atom and f_j is the scattering factor for the electron. This scattering factor is derived from the Thomson classical scattering of x-rays by the electron.¹

The x-rays incident upon the atom give rise to an oscillating electronic dipole movement which radiates x-rays. To get the total amplitude scattered by the j^{th} electron, the dipole radiation scattered from the fraction of the j^{th} electron in the volume increment dv is summed over all space taking into account the path length differences between the elements dv . Therefore,

$$f_j = \int D_j f_j \exp(i\phi) dv$$

where ϕ is the phase angle depending upon the angle of scattering, ρ is the number of electrons in the element dv . D_j is the amplitude scattered by that charge. D_j is dependent on electron type only so it may be taken out of the integral. This gives

$$f_j = D_j f_j^0 \quad \text{where} \quad f_j^0 = \int \rho \, dv$$

Parratt and Hempstead¹² showed that

$$D_j = (1 + \xi_j + i \eta_j) = \int_{\omega_j}^{\infty} \frac{W_j(\omega) \, d\omega}{\omega_j^2 - (\omega/\omega_0)^2 - i (K_j/\omega_0)}$$

where ω is the angular frequency of a virtual oscillation associated with the j^{th} electron, for which there are $W_j(\omega)d\omega$ oscillators in the frequency range $d\omega$, ω_0 is the incident x-ray frequency, ω_j is the frequency of the j^{th} electron absorption edge, and K_j is a damping constant. Combining the two expressions for f_j and the expression for D_j then

$$\Delta f'' = \sum_j Z_j n_j f_j^0$$

Next n_j must be found for each electron. Again from Parratt and Hempstead's¹² treatment of anomalous dispersion it is found that for Cu K α radiation

$$(2) \quad \sum_j n_j = \left(\pi/2\right) g_j \left(\lambda/\lambda_j\right)^{p_j-1} (P_{j-1}) \quad \lambda_j > \lambda$$

$$\sum_j n_j = 0 \quad \lambda_j < \lambda$$

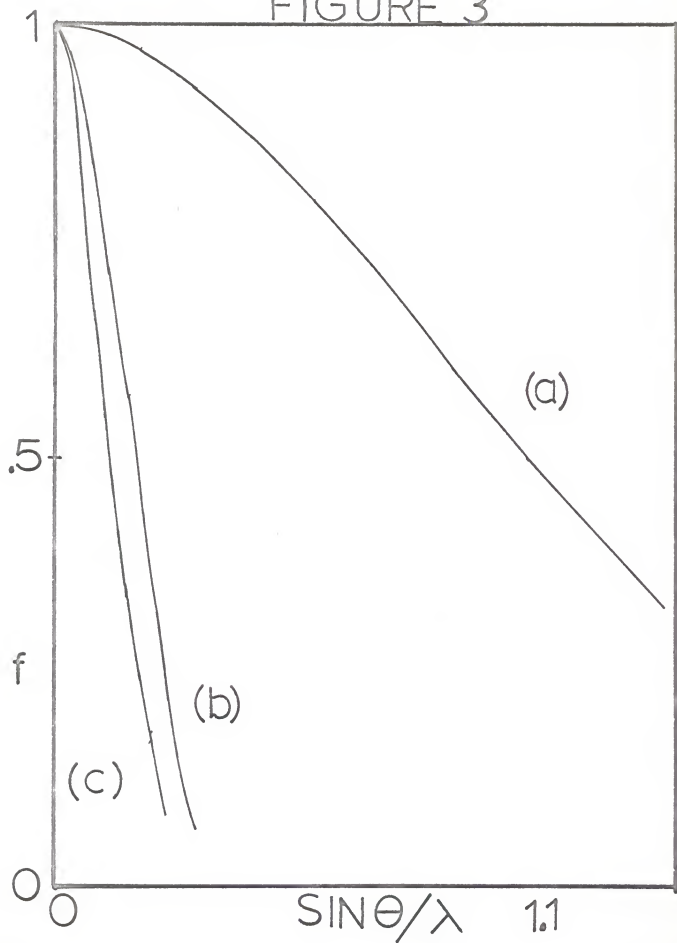
where g_j is the oscillator strength for all the j electrons, λ_j is the absorption edge wavelength and $P_j = 11/4, 2, 5/2, 5/2$ for the K, L_1 , L_2 , L_3 and M absorption edges, respectively. The values of f_j for the various electrons in calcium, carbon, and oxygen were obtained from three papers by Freeman,¹⁵ (Ca, O) and Keating and Vineyard¹⁵ (C). The values for f_K , f_{L_1} , $f_{L_{2,3}}$, and f_M are plotted for several values of $(\sin \theta/\lambda)$, see figures 3, 4, and 5. The theoretical calculations of epsilon for the 211 plane is used to illustrate the procedure.

As will be shown later, the crystal structure factor for the 211 plane

EXPLANATION OF FIGURE 3

Incoherent scattering curve for carbon (a) is the f_k scattering curve (b) is the f_{L_1} scattering curve (c) is the $f_{L_2,3}$ scattering curve.

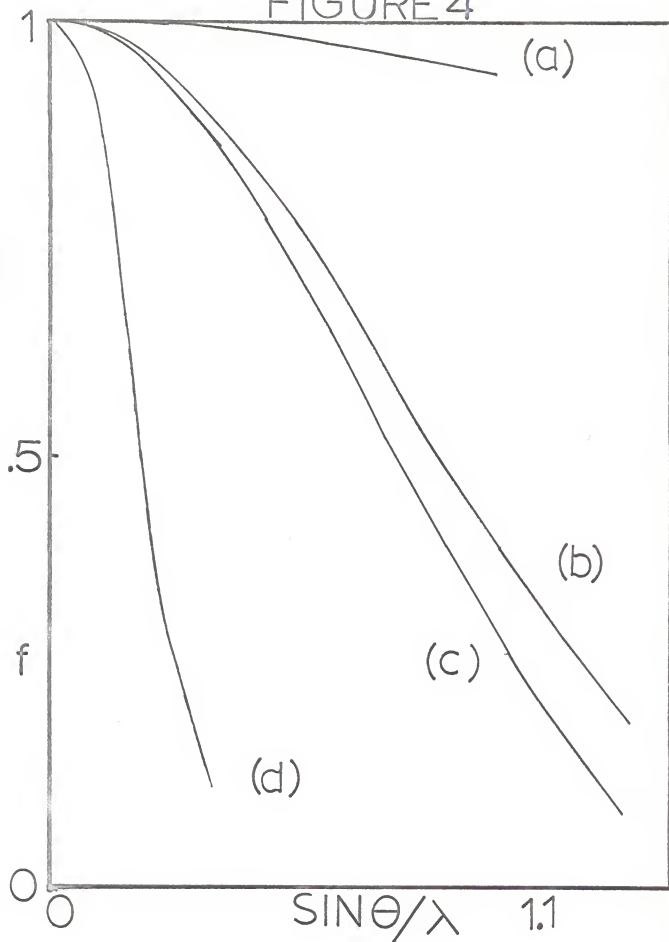
FIGURE 3



EXPLANATION OF FIGURE 4

Incoherent scattering curve for calcium
(a) scattering curves for $f(k)$ (b) scattering curve for $f_{L_2,3}$
(c) scattering curves for f_{L_1} (d) scattering curve for $f_{N_2,3}$

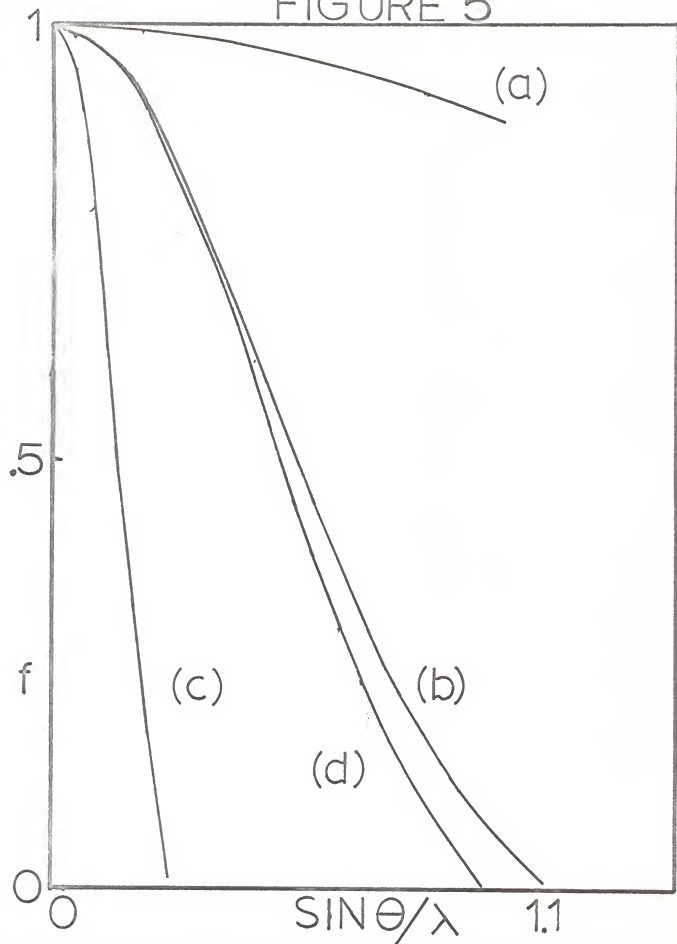
FIGURE 4



EXPLANATION OF FIGURE 5

Incoherent scattering curve for oxygen (a) scattering curve for f_k
(b) scattering curve for $f_{L_2,3}$ (c) scattering curve for f_{L_1} (d) scattering
curve for f_M .

FIGURE 5



of calcite is given by

$$F_{211} = 2(f_{Ca} + f_C + f_O) \text{ and } \frac{\sin \Theta}{\lambda} = \frac{1}{2d} = \frac{1}{6.07} = 0.1647$$

The atomic scattering factors are written in terms of their real and complex

$$\text{parts so } F_{211} = 2 \left\{ \underbrace{(f_{Ca}^r + f_C^r + f_O^r)}_{F_H'} + i \underbrace{(\Delta f_{Ca}'' + \Delta f_C'' + \Delta f_O'')}_{F_H''} \right\}$$

$$(3) \text{ so } F_{211}'' = 2 (\Delta f_{Ca}'' + \Delta f_C'' + \Delta f_O'')$$

$$\Delta f_{Ca} = (Z_N n_N)_{Ca} (f_N)_{Ca} + (Z_{L1} n_{L1} f_{L1})_{Ca}$$

$$\Delta f_C = (Z_N n_N)_C (f_N)_C + (Z_{L1} n_{L1} f_{L1})_C + (Z_{L2,3} n_{L2,3} f_{L2,3})_C$$

$$\Delta f_O = (Z_N n_N f_N)_O + (Z_{L1} n_{L1} f_{L1})_O + (Z_{L2,3} n_{L2,3} f_{L2,3})_O$$

$$+ (Z_m n_m f_m)_O$$

The values for these parameters are found from table 1 and figures 3, 4, and

5.

$$\Delta f_{Ca}'' = 1.091 \times 0.998 + 0.1471 \times 0.968 + 0.859 \times 0.974 + 0.0006 \times 0.7$$

$$\Delta f_C'' = 0.0104 \times 0.982 + 0.0012 \times 0.579 + 0.000053 \times 0.446$$

$$\Delta f_O'' = 0.0102 \times 0.990 + 0.0108 \times 0.746 + 0.00034 \times 0.630$$

$$\Delta'' f_{Ca} = 1.317$$

$$\Delta'' f_C = 0.01093$$

$$\Delta'' f_O = 0.01835$$

$$\text{thus, } F_{211}'' = 2.692$$

$$\epsilon_{211} = \frac{F_{211}''}{F_{000}''}$$

From table 2

TABLE 1
ELECTRON FORM FACTORS

Ca ⁺² (18 electrons)			O ⁻² (10 electrons)			C (6 electrons)		
K	I _T	L _{2,3}	M	K	I _T	L _{2,3}	K	I _T
1.091	0.1471	.0859	0.0006	0.0102	0.0108	.00034	0.0104	0.0012
								0.000053

TABLE 2: CHART OF THE CRYSTAL STRUCTURE FACTORS

F_{hkl}	$h + k + l$	$m \text{ or } s$	h	p	l	q	$\frac{h + l}{2}$
$2(f_{ca} + f_c + 3f_o)$	E	E	E	E	E	E	
$2(f_{ca} + f_c - f_o)$	E	E	E	O	E	E	
$2(f_{ca} + f_c - f_o)$	E	E	E	E	E	O	
$2(f_{ca} + f_c - f_o)$	E	E	E	E	O		
$2(f_{ca} + f_c + f_o)$	E	E	E	O	O		
$2(f_{ca} + f_c - f_o)$	E	E	O		E	E	
$2(f_{ca} + f_c + f_o)$	E	E	O		E	O	
$2(f_{ca} + f_c - f_o)$	E	E	O		O		E
$2(f_{ca} + f_c + f_o)$	E	E	O		O		O
$2(f_{ca} - f_c - 3f_o)$	E	O	E	O	E	O	
$2(f_{ca} - f_c + f_o)$	E	O	E	O	E	E	
	E	O	E	E	E	O	
	E	O	E	E	E	E	
O	O	u or v	E	E	E	E	
$-4f_o$	O	u or v	E	O	E	E	
$4f_o$	O	u or v	E	E	E	O	
O	O	u or v	E	O	E	O	
O	O	u or v	O		O		
O	O	u	E	E	u		
O	O	u	E	O	u		
$-4f_o$	O	u	E	E	v		
$4f_o$	O	u	E	O	v		
$-4f_o$	O	v	E	E	u		

TABLE 2: CHART OF THE CRYSTAL STRUCTURE FACTORS (continued)

F_{hkl}	$h + k + l$	m or s	h	p	l	q	$\frac{h + l}{2}$
$4f_o$	0	v	E	O	u		
0	0	v	E	E	v		
0	0	v	E	O	v		
0	0	u	u		E	E	
0	0	u	u		E	O	
$4f_o$	0	u	v		E	E	
$-4f_o$	0	u	v		E	O	
$4f_o$	0	v	u		E	E	
$-4f_o$	0	v	u		E	O	
0	0	v	v		E	E	
0	0	v	v		E	O	

F_{hkl}	$h + k + l$	m	h	p	l	q	$\frac{h + l}{2}$
$2(f_{ca} - f_c + f_o)$	E	O	E	E	E	E	
$2(f_{ca} - f_c + f_o)$	E	O	E	E	E	O	
$2(f_{ca} - f_c + f_o)$	E	O	E	O	E	E	
$2(f_{ca} - f_c - f_o)$	E	O	E	E	O		
$2(f_{ca} - f_c + f_o)$	E	O	E	O	O		
$2(f_{ca} - f_c - f_o)$	E	O	O		E	E	
$2(f_{ca} - f_c + f_o)$	E	O	O		E	O	
$2(f_{ca} - f_c - f_o)$	E	O	O		O		O

TABLE 2: CHART OF THE CRYSTAL STRUCTURE FACTORS (continued)

F_{hkl}	$h + k + l$	m	h	p	l	q	$\frac{h + l}{2}$
$2(f_{ca} - f_c + f_o)$	E	O	O		O		E
$2(f_{ca} + f_c - f_o)$	E	E	E	O	E	O	

$$\begin{aligned}
F_{000} &= 2(f_{Ca} + f_C + 3f_O) \\
F_{000} &= 2 \left\{ (n_K z_K f_K)_{Ca} + (n_{Li} z_{Li} f_{Li})_{Ca} + (n_{Li,3} z_{Li,3} f_{Li,3})_{Ca} \right. \\
&\quad (n_m z_m f_m)_{Ca} + (n_K z_K f_K)_C + (n_{Li} z_{Li} f_{Li})_C \\
&\quad + (n_{Li,3} z_{Li,3} f_{Li,3})_C + 3[(n_K z_K f_K)_O + (n_{Li} z_{Li} f_{Li})_O \\
&\quad \left. + (n_{Li,3} z_{Li,3} f_{Li,3})_O + (n_m z_m f_m)_O] \right\}
\end{aligned}$$

Since for $(hkl) = (000)$, $\frac{\sin \theta}{\lambda} = 0$, then all the incoherent scattering factors are 1 so

$$\begin{aligned}
F_{000}'' &= 2 \{ 1.0910 + 0.1471 + 0.0859 + 0.0006 + 0.0104 \\
&\quad + 0.0012 + 0.0001 + 3(0.0102 + 0.0108 + 0.0003) \} = 2.800
\end{aligned}$$

Thus,

$$\varepsilon_{211} = \frac{F_{211}''}{F_{000}''} = \frac{2.692}{2.800} = 0.961$$

Table 3 has the other values of epsilon calculated for this crystal using this method.

TABLE 3
CALCULATED VALUES OF EPSILON

ε_{0211}	0.961
ε_{0310}	0.919
ε_{0112}	0.919
$\varepsilon_{010\bar{1}}$	0.931
ε_{0213}	0.934
ε_{0423}	0.0194

The previous calculation of epsilon was based on the solution of Maxwell's equations for the x-ray case. Epsilon can be calculated by a different procedure which is based on the absorption coefficient of each individual atom in the crystal. If the total electron field in the crystal is considered as being the vector sum of the incident and diffracted beams, then

$$|\mathcal{E}|^2 = E_0^2 + E_H^2 + 2E_0 \cdot E_H \exp(-2\pi i \mathbf{H} \cdot \mathbf{r})$$

Referring to Figure 6, let \mathbf{r}_0 be the position of the nucleus of an atom in the wave field and \mathbf{r} the vector to the volume dv . Let $\mu(\mathbf{r}_a)dv$ be the contribution of the element dv to the average absorption coefficient of the atom. Let $\mu = \int \mu(\mathbf{r}_a)dv$ be the average absorption coefficient of the atom. If it is assumed that the absorption coefficient at any point is proportional to $|\mathcal{E}|^2$, the absorption coefficient of the atom at \mathbf{r}_0 in the field can be written as

$$\begin{aligned} \mu(\mathbf{r}_0) &= T \int \mathcal{E}^2(\mathbf{r}) \mu(\mathbf{r}_a) dv \\ &= T \left\{ (E_0^2 + E_H^2) \int \mu(\mathbf{r}_a) dv + 2E_0 \cdot E_H \int \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \mu(\mathbf{r}_a) dv \right\} \\ &= T \left\{ (E_0^2 + E_H^2) \mu + 2E_0 \cdot E_H \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_0) \int \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_a) \mu(\mathbf{r}_a) dv \right\} \end{aligned}$$

where the integral is over the volume of the atom and T is a proportionality constant. If this value of $\mu(\mathbf{r}_0)$ is found for each position in the crystal, an averaged μ results. If the last integral is abbreviated $\frac{\mu_H}{\mu}$, then

$$\mu = \mu_0 \left(1 \pm P \frac{2|E_0||E_H|}{E_0^2 + E_H^2} \frac{\mu_{0H}}{\mu_0} \right)$$

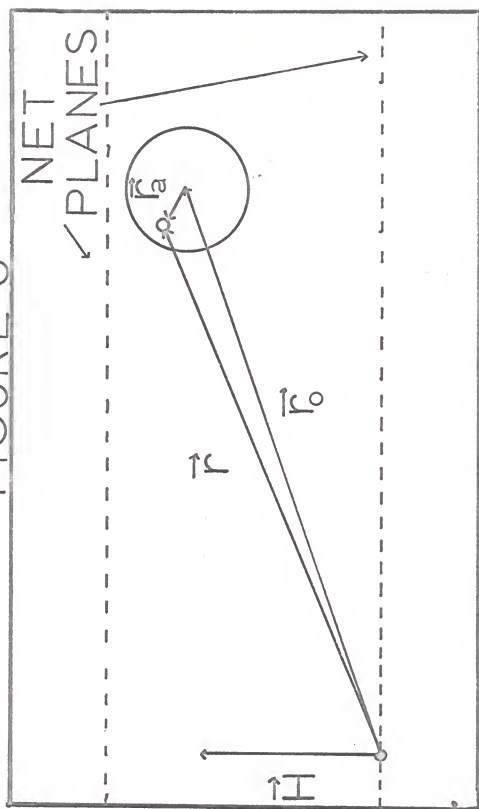
The formal theory yields

$$\mu = \mu_0 \left(1 \pm |P| \frac{2|E_0||E_H|}{E_0^2 + E_H^2} \epsilon \right)$$

EXPLANATION OF FIGURE 6

Geometry used to calculate the absorption of an atom in the x-ray wave field.

FIGURE 6



The similarity makes it desirable to equate ϵ and $\frac{\mu_{\text{OH}}}{\mu_0}$, and as it is defined, ϵ is related to the weighted distribution of absorbing power within the atom.

To calculate ϵ consider

$$\begin{aligned} (5) \quad \epsilon &= \frac{\mu_{\text{OH}}}{\mu_0} = \frac{1}{\mu_0} \int \exp(i\pi \mathbf{r} \cdot \mathbf{H} \cdot \mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{\mu_0} \sum_j \exp(i\pi \mathbf{r}_j \cdot \mathbf{H} \cdot \mathbf{r}_j) \rho(\mathbf{r}_j) \end{aligned}$$

where j 's are summed over all atom positions. As an example, ϵ for the 211 plane of calcite is calculated here.

From Wyckoff¹³ the following positions for the atoms in calcite are obtained

$$\begin{aligned} \text{Ca } (0 \ 0 \ 0, 1/2 \ 1/2 \ 1/2) \quad \text{C } (1/4 \ 1/4 \ 1/4, 3/4 \ 3/4 \ 3/4) \\ \text{O } (0 \ 1/2 \ 3/4; 1/2, 3/4, 0; 3/4, 0, 1/2; \\ 0, -1/2, -3/4; -1/2, -3/4, 0; \\ -3/4, 0, -1/2) \end{aligned}$$

For 211, $\underline{H} \cdot \underline{r}$ for each atom is calculated where $\underline{H} = 2b_1 + 2b_2 + 2b_3$ and \underline{r} 's are given above

$$\underline{H} \cdot \underline{r} = \begin{pmatrix} \text{Ca} & \text{C} & \text{O} \\ 0 & 1 & 5/4 & -5/4 \\ 2 & 3 & 7/4 & -7/4 \\ & & 2 & -2 \end{pmatrix}$$

The equation for epsilon is given in terms of absorption coefficients per atom, whereas available data are in terms of absorption coefficients per unit mass, so a conversion from one set of units to the other is necessary.

The mass absorption coefficient for a particular atom type is

$$\begin{aligned}\mu_{ma} &= \mu_a \left(\frac{\text{no. molecules}}{\text{mole}} \right) \left(\frac{\text{mole}}{\text{gram}} \right) \\ &= \mu_a \frac{N_0}{(\text{A.t. Wt.})_a} \\ \mu_a &= \frac{(\text{A.t. Wt.})_a}{N_0} \mu_{ma}\end{aligned}$$

Since the absorption coefficient is in terms of mass absorption coefficients, these can be substituted in the equation for the atomic absorption

coefficients.

$$\begin{aligned}\mu_a &= \sum_1^3 \frac{(\text{A.t. Wt.})_{c_a}}{N_0} \mu_{ma_{c_a}} + \sum_1^2 \frac{(\text{A.t. Wt.})_c}{N_0} \mu_{ma_c} + \sum_1^6 \frac{(\text{A.t. Wt.})_{c_o}}{N_0} \mu_{ma_{c_o}} \\ \mu_{aH} &= \sum_{j=1}^3 \frac{(\text{A.t. Wt.})_{c_a}}{N_0} \mu_{ma_{c_a}} \exp(2\pi^2 H \cdot n_j^2) + \sum_{j=1}^2 \frac{(\text{A.t. Wt.})_c}{N_0} \mu_{ma_c} \exp(2\pi^2 H \cdot n_j^2) \\ &\quad + \sum_{j=1}^6 \frac{(\text{A.t. Wt.})_{c_o}}{N_0} \mu_{ma_{c_o}} \exp(2\pi^2 H \cdot n_j^2) \\ (6) \epsilon &= \frac{\mu_{aH}}{\mu_a} = \frac{\sum_1^3 A_{c_a} \mu_{ma_{c_a}} \exp(2\pi^2 H \cdot n_j^2) + \sum_1^2 A_c \mu_{ma_c} \exp(2\pi^2 H \cdot n_j^2) + \sum_1^6 A_{c_o} \mu_{ma_{c_o}} \exp(2\pi^2 H \cdot n_j^2)}{2 (A_{c_a c_o_3} \mu_{ma_{c_a c_o_3}})}\end{aligned}$$

As an example, the calculated value of ϵ for the 211 plane using Cullity's⁴ value for mass absorption coefficient

$$\epsilon = \frac{(40 \times 172)(2) + (12 \times 5.5)(2) + (16 \times 12.7)(6)}{7556} = 0.942$$

THE EXPERIMENT

In order for a wave field to be established in the crystal, the structure of the crystal must be very nearly perfect. If there is an imperfection, either a foreign element or a strain producing a change in d-spacing different from the rest of the crystal, then the constructive interference necessary for anomalous transmission will not occur.

Several crystals upon which similar experiments have been done have been synthetically produced. These crystals exhibit a high degree of perfection. To date no synthetic crystals of calcite have been produced large enough for the present research. Consequently, a naturally occurring calcite crystal had to be used for this experiment. Rather good calcite samples were procured from J. A. Bearden¹⁶ (Johns Hopkins University).

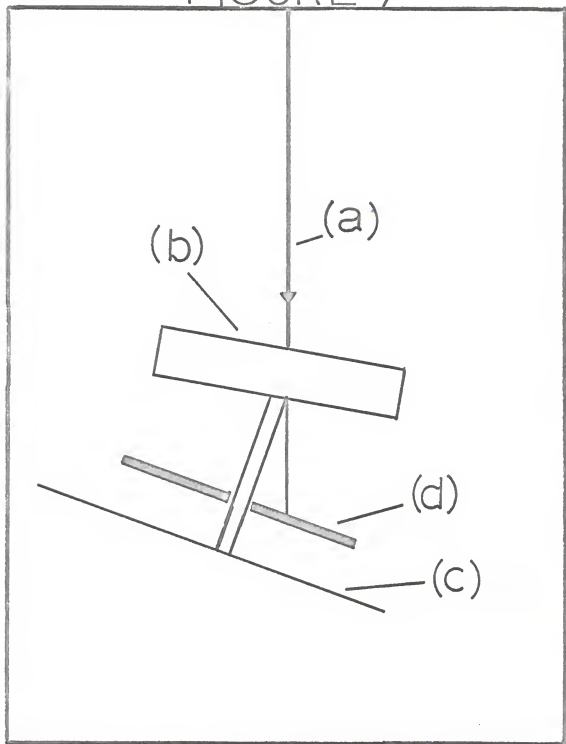
The determination of the perfection of a crystal is made using the Lang Topographs. In the Lang technique, the crystal is placed on a camera that allows the crystal to be translated. The film holder is also attached to the movable slide. Between the crystal and the film there is a vertical slit. The slit is stationary with respect to the camera and x-ray beam. Referring to the figure 7, if the crystal translates as is shown and the camera is set at the proper angle such that the Bragg condition is satisfied, then a one to one mapping of the crystal will be made onto the film. Wherever there is an imperfection in the crystal, a dark area will appear on the film. The reason that a dark area appears wherever there is an imperfection is due to the break down of first order or primary extinction. A good explanation of the Lang topograph is given by Lang.⁹

Topographs of three calcite crystals are shown in figures 8, 9, 10, and 11. The first few crystals were quite imperfect, notably the B and L

EXPLANATION OF FIGURE 7

A collimated x-ray beam (a) strikes the crystal (b), set at the proper angle for Laue diffraction. The diffracted beams hit the film (c) placed close to the crystal. Crystal and film move back and forth together during the exposure, both being mounted on a slide; the direction of motion being parallel to the crystal slice. The stationary screen (d) prevents the direct beam from reaching the film.

FIGURE 7



EXPLANATION OF FIGURES 8, 9, 10, and 11.

Fig. 8. Topograph of a crystal which shows a great amount of lattice strain.

Fig. 9. Topograph of a near perfect Argentine calcite crystal before polishing. Cleavage on surfaces is apparent.

Fig. 10. Topograph of an Argentine crystal after rough polishing. Surface scratches are clearly visible.

Fig. 11. Topograph of the same crystal as shown in fig. 10 but after final polishing. The crystal in this condition was used to obtain the data for this study.

Fig 8



Fig 9



Fig 10



Fig 11



crystal, figure 8. However, after a few trials it was noticed that the imperfection that appeared in the Argentine crystals followed the basic contour of the surface. Consequently, it was decided that an attempt should be made to polish the crystal.

To do this polishing, a Buehler polishing apparatus was used, see figures 12, 13, 14 and 15. In this unit the crystal is mounted on the five holed wheel. Wooden blocks were inserted in the hole in order that the crystal could be glued to it. The five holed piece was placed on the polishing wheel and the driving mechanism was placed over this. The driving gear counterrotated the sample wheel as the polish progressed. The Buehler instruction manual calls for a pressure of fifty to sixty pounds to be placed on the wheel. However, it was realized rapidly that this was impractical since cloths were ripped and crystals cracked. Consequently, all crystals were polished without adding to the pressure developed by the weight of the wheel.

The crystals were brought down to the desired thickness using No. 600 grit paper. The rough polishing was accomplished first with Billiard cloth and 6 micron aluminum oxide polish, followed by micron cloth and 1 micron aluminum oxide. The final polish was with 0.05 micron Gamma Alumina on a velvet cloth. The entire procedure took approximately two hours per crystal and produced a highly polished surface. Some of the crystals were etched, but this did not show up on the topograph, so the later crystals were not etched.

After the polishing, several crystals exhibited almost perfect topographs, figure 11. The perfect topograph has only the edge of the crystal apparent, and the center of the crystal is either clear or, at least,

EXPLANATION OF FIGURES 12, 13, 14, and 15.

Fig. 12. The Buehler polishing table.

Fig. 13. The automatic polishing apparatus.

Fig. 14. The crystal mounting wheel.

Fig. 15. The entire assembly ready to polish a crystal.

Fig 12



Fig 13



Fig 14

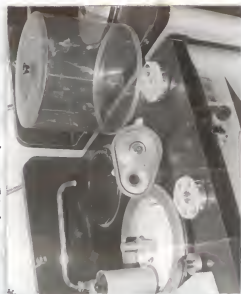


Fig 15



contains a uniform light density. Only crystals that exhibited this condition and were of sufficient size to be handled easily (approximately 1 cm²) were used.

As was stated earlier, in order that a crystal exhibit anomalous transmission, it must have a $\mu_o t \gg 1$ that is, the linear absorption coefficient times the thickness must be much greater than one. However, it should not be too large because

$$I = I_0 \exp(-\mu_o t [1 - \epsilon])$$

so if $\mu_o t$ is too large, say on the order of 15, then only x-rays from extremely strong diffracting planes with values of $\epsilon \approx 1$ will be seen. As it was desired to work with several planes of low ϵ , a $\mu_o t$ of about five was desired. With this in mind, a 0.513 mm crystal was chosen for calcite in CuK α radiation and a 2.58 mm crystal was chosen for the MoK α radiation.

DETERMINATION OF THE PLANES IN CALCITE TO INVESTIGATE

Of particular importance as regards the planes chosen for this experiment, are (1) the crystal structure factor for the plane, and (2) the angle between a particular plane and the other planes in the crystal. The crystal structure factor is defined by the equation

$$(8) \quad F(hkl) = \sum_i^N f_n \exp(2\pi i [h u_n + k v_n + l w_n])$$

where hkl are the Miller indices for the plane, f_n are the atomic scattering factors for the various atoms in the crystal, and u_n , v_n and w_n are the position of the various atoms in the unit cell of the crystal.

For calcite the atoms in the lattice have the following positions

CA			C			O		
0	0	0	1/4	1/4	1/4	0	1/2	3/4
1/2	1/2	1/2	3/4	3/4	3/4	1/2	3/4	0
						3/4	0	1/2
						0	-1/2	-3/4
						-1/2	-3/4	0
						-3/4	0	-1/2

Substituting these values in equation 8 for u , v and w

$$\begin{aligned} F_{hkl} = & f_{Ca} \left[\exp(2\pi i [0h + 0k + 0l]) + \exp(2\pi i [\frac{1}{4}h + \frac{1}{4}k + \frac{3}{4}l]) \right] \\ & + f_C \left[\exp(2\pi i [\frac{3}{4}h + \frac{3}{4}k + \frac{3}{4}l]) + \exp(2\pi i [\frac{1}{2}h + \frac{3}{4}k + \frac{3}{4}l]) \right] \\ & + f_O \left[\exp(2\pi i [0h + \frac{1}{2}k + \frac{3}{4}l]) + \exp(2\pi i [\frac{1}{2}h + \frac{3}{4}k + 0l]) \right] \\ & + f_O \left[\exp(2\pi i [\frac{3}{4}h + 0k + \frac{1}{2}l]) + \exp(2\pi i [0h + \frac{1}{2}k + \frac{1}{4}l]) \right] \\ & + f_O \left[\exp(2\pi i [\frac{1}{4}h + 0k + \frac{1}{2}l]) + \exp(2\pi i [\frac{1}{2}h + \frac{1}{4}k + 0l]) \right] \end{aligned}$$

When these are reduced, the expression becomes

$$F_{hkl} = \left[f_{ca} + f_c e^{\frac{\pi i}{2} (h+k+l)} \right] \left[1 + e^{\pi i (h+k+l)} \right] \\ + 2 f_0 \left[\cos \pi \left(k + \frac{3}{2} l \right) + \cos \pi \left(h + \frac{3}{2} k \right) + \cos \pi \left(\frac{3}{2} h + l \right) \right]$$

using the relation $\cos(A+B) = \cos A \cos B - \sin A \sin B$

$$F_{hkl} = \left[f_{ca} + f_c e^{\frac{\pi i}{2} (h+k+l)} \right] \left[1 + e^{\pi i (h+k+l)} \right] \\ + 2 f_0 \left\{ (-1)^k \cos \frac{3}{2} l \pi + (-1)^h \cos \frac{3\pi}{2} k + (-1)^l \cos \frac{3\pi}{2} h \right\}$$

Let $h + k + l = 2m$ $k = 2m = l - h$

$$F_{hkl} = \left[f_{ca} + f_c e^{\pi m i} \right] \left[1 + e^{2\pi m i} \right] + \\ + 2 f_0 \left\{ (-1)^{2m-h-l} \cos \frac{3\pi l}{2} + (-1)^h \cos \frac{3\pi}{2} (2m-l-h) + (-1)^l \cos \frac{3\pi}{2} h \right\}$$

Let us look at $h + k + l = 2m$. The magnitude of m is unimportant; however, whether it is odd or even is important. Three conditions can hold:

- If h is even, l is odd and k is odd.
- If h is even, l is even and k is even.
- If h is odd, l is odd and k is even.

But we notice that this is the same behavior as exhibited by $h + l$, so $2m - h - l$ may be replaced by $h + l$ everywhere except in the cosine terms. To deal with these possible variations, the cosine terms were expanded

$$\cos \frac{3\pi}{2} (2m-h-l) = \cos \frac{3\pi}{2} m \cos (h+l) \frac{3\pi}{2} = (-1)^m \cos (l+h)$$

so

$$F_{hkl} = 2 \left\{ f_{ca} + f_c e^{\pi m i} \right\} + 2 f_0 \left\{ (-1)^{h+l} \cos \frac{3\pi}{2} \right. \\ \left. + (-1)^{h+m} \cos \frac{3\pi}{2} (h+l) + (-1)^l \cos \frac{3\pi}{2} h \right\}$$

From this point it is a matter of combining the conditions

$$h + k + l = \begin{cases} \text{even} & h + k + l = 2n, \quad m \begin{cases} \text{even} \\ \text{odd} \end{cases} \\ \text{odd} & \begin{cases} h + k + l = S = (1, 5, 9, 13, \dots) = u \\ h + k + l = S = (3, 7, 11, \dots) = v \end{cases} \end{cases}$$

$$\begin{aligned} h & \begin{cases} \text{even} & h = 2P, P \begin{cases} \text{even} \\ \text{odd} \end{cases} \\ \text{odd} \end{cases} \\ l & \begin{cases} \text{even} & l = 2q, q \begin{cases} \text{even} \\ \text{odd} \end{cases} \\ \text{odd} \end{cases} \end{aligned}$$

DETERMINATION OF ANGLES BETWEEN PLANES

Calcite is rhombohedral in structure. This implies that the three periodic distances are equal, i.e., $a_1 = a_2 = a_3$, and the angles between the cell axes are the same. For calcite the angle is $46^{\circ}07'$ and a , the periodic distance, is 6.361 \AA . When dealing with a crystal, it is easier to examine the reciprocal lattice rather than the natural lattice. In the reciprocal lattice, each plane of the crystal is represented by a vector H , which is perpendicular to the plane and has magnitude equal to $\frac{1}{d}$ for that plane. A periodic distance in reciprocal lattice is defined as

$$(9) \quad b_i = \frac{a_j \cdot a_k}{a_i \cdot a_j \cdot a_k}$$

Since the natural lattice is not cubic, tetragonal or orthorhombic neither is the reciprocal lattice. Consequently, the primary axes are not orthogonal and $b_1 \cdot b_2 \neq |b_1| |b_2|$. In order to calculate angles between planes it was first necessary to find the angle between the primary axes in the reciprocal lattice. This computation was carried out in the following manner.

From geometrical consideration the scalar product between $b_1 \cdot b_2$ for a rhombohedral parallelepiped is

$$b_1 \cdot b_2 = \frac{(\cos^2 \alpha - \cos \alpha)}{a^2(1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha)}$$

since the magnitude of $b_1 = b_2 = b_3$, then $b_1 \cdot b_2 = b_1^2 \cos \alpha$ where α is the angle between b_1 and b_2 .

$$b_1 \cdot b_1 = b_1^2 = \frac{\sin^2 \alpha}{a^2(1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha)}$$

so

$$(10) \quad \cos \alpha = \frac{-\cos \alpha}{1 + \cos \alpha} = -0.409$$

With this information the interplanar angles were determined.

To compute the angles between the various planes, the scalar products between the various planes were considered.

$$\begin{aligned} H(hkl) \cdot H(h'k'l') &= (hb_1 + kb_2 + lb_3) \cdot (h'b_1 + k'b_2 + l'b_3) \\ &= hh'b_1 \cdot b_1 + kk'b_2 \cdot b_2 + ll'b_3 \cdot b_3 \\ &\quad + hk'b_1 \cdot b_2 + hl'b_1 \cdot b_3 + kl'b_2 \cdot b_1 \\ &\quad + kl'b_2 \cdot b_3 + lh'b_1 \cdot b_3 + lk'b_3 \cdot b_2 \\ &= hh'b_1^2 + kk'b_2^2 + ll'b_3^2 + hk'(b_1^2)(-0.409) + hl'(b_1^2)(-0.409) \\ &\quad + kh'(b_1^2)(-0.409) + kl'(b_1^2)(-0.409) + lh'(b_1^2)(-0.409) \\ &\quad + lk'(b_1^2)(-0.409) \\ H_{hkl} \cdot H_{h'k'l'} &= \{ (hh' + kk' + ll') + \{hk' + hl' + kh' + kl' + lh' + lk'\} \\ &\quad \{-0.409\} \} b_1^2 \end{aligned}$$

$$\text{but } H_{hkl} \cdot H_{h'k'l'} = |H_{hkl}| |H_{h'k'l'}| \cos \phi$$

$$\cos \phi = \frac{H_{hkl} \cdot H_{h'k'l'}}{|H_{hkl}| |H_{h'k'l'}|}$$

$$\begin{aligned} |H_{hkl}| &= \{ h^2 b_1^2 + k^2 b_2^2 + l^2 b_3^2 + 2hkb_1 \cdot b_2 + 2hlb_1 \cdot b_3 + 2klb_2 \cdot b_3 \}^{1/2} \\ &= b_1 \{ h^2 + k^2 + l^2 + (-0.409)(2hk + 2hl + 2kl) \}^{1/2} \end{aligned}$$

$$\cos \phi =$$

$$\frac{[\{hh'kk'+ll'\} + \{hk'+hl'+kk'+kl'+lh'+lk'\} \{-0.409\}]}{\{h^2+k^2+l^2+(-0.409)(2)(hk+hl+kl)\}^{1/2} \{h'^2+k'^2+l'^2+(-0.409)(2)(h'k'+h'l'+k'l')\}^{1/2}}$$

As an example, the angle between the (211) and (121) planes is

$$\cos \phi = \frac{[\{2+2+1\} + \{4+2+1+1+1+2\} \{-0.409\}]}{\{4+1+1+(-0.409)(2)(2+2+1)\}^{1/2}} = \frac{0.5}{1.91}$$

$$\text{so } \phi = 75.4^\circ$$

When choosing the planes to examine, two criteria were taken into consideration. First, it is desired that the crystal structure factors be different so that an attempt could be made to isolate contributions of the individual atoms. Since the Debye Waller factor contains a vibration constant, it was desired that the reciprocal lattice vectors chosen be almost parallel, that is, the angles between them be small. With these criteria in mind and also considering intensities of diffraction, the 211, 422, 423, 301, $10\bar{1}$, and 213 planes were chosen.

X-RAY DIFFRACTION TECHNIQUES

In order to determine experimentally epsilons for the planes in calcite, the crystal had to be aligned in such a manner that the reciprocal lattice vector for the desired plane lay in the plane of incidence of the x-rays; that is, the plane defined by the intersection of the incident beam and the diffracted beam. In addition, the reciprocal lattice vector must be at such an angle that it bisects the angle between the incident and diffracted beams. In order to do this, the previously determined angle between the face planes and each reciprocal lattice vector were used.

The crystal was oriented such that the face plane 121 was perpendicular to the x-ray beam when the diffractometer was set for zero degrees. The crystal was rotated fifteen degrees (the complement of the angle between the 121 and the 211). Next the diffractometer was set on the Bragg angle for the 211. Then, without a slit or collimator on the detector, the angle χ was varied until the diffraction maximum was reached. At this point a collimator and slit were placed on the detector, and the angle Ω was varied to obtain a maximum. The crystal was then aligned for diffraction from both the $k\alpha$ and the $k\lambda$ wavelengths of the radiation. The diffractometer was motor driven to rotate through all Bragg angles at a rate of 0.2 degrees per minute. The areas of the graphs for the intensity diffracted by $k\alpha$ and $k\lambda$ wavelengths for each set of planes were the data from which epsilon was calculated.

The same slit was not used for every plane. For most, the 0.1 degree slit was used, but for the very weakly diffracting planes, the 0.3 degree slit was used. This was done since the very weak planes did not have sufficient intensity to be counted with the 0.1° slit. Since the ratio of

the areas under the $k\alpha$ and $k\beta$ diffracted peaks was not affected by the size of the slit, there was nothing lost in going to the larger slit.

In order that the diffraction graphs be limited to the $k\alpha$ and $k\beta$ radiation only, the base line on the pulse height analyzer was set so that the $k\alpha$ line was just barely clipped. This insured that no wavelength longer than the $k\alpha$ was counted. The window was closed down until the $k\beta$ line was just barely clipped. This insured that no wavelength shorter than the $k\beta$ was counted.

In the data analysis it was necessary to measure the area of the intensity curves for the incident $k\alpha$ and $k\beta$ radiations, $I_{0\alpha}$ and $I_{0\beta}$, respectively, and take their ratios. To obtain this, a powdered quartz sample was used. The Bragg diffraction peaks for the most intensely diffracting planes of quartz powder were used. The ratio of the incident intensity of the $k\alpha$ and $k\beta$ wavelengths ($I_{0\alpha}/I_{0\beta}$) are related to the area under the graphs of the powder quartz sample by the equation

$$(11) \quad \frac{A_{\alpha}}{A_{\beta}} = \frac{I_{0\alpha}}{I_{0\beta}} \left(\frac{1 + \cos^2 2\theta_{\alpha}}{\sin^2 \theta_{\alpha} \cos \theta_{\alpha}} \right) \left(\frac{1 + \cos^2 2\theta_{\beta}}{\sin^2 \theta_{\beta} \cos \theta_{\beta}} \right)$$

where A_{α} and A_{β} are the areas under the $k\alpha$ and $k\beta$ Bragg reflections, respectively, θ_{α} and θ_{β} are the Bragg angles for the respective wavelengths in quartz, and $I_{0\alpha}$ and $I_{0\beta}$ are the intensity of the incident $k\alpha$ and $k\beta$ wavelengths, respectively.

ANALYSIS OF DATA

In the analysis of data the following terms were used:

$$t_{\alpha} = t_0 \left[\frac{1}{\sin(\theta_{\alpha} + A)} + \frac{1}{\sin(A - \theta_{\alpha})} \right]$$

$$t_{\beta} = t_0 \left[\frac{1}{\sin(\theta_{\beta} + A)} + \frac{1}{\sin(A - \theta_{\beta})} \right]$$

θ_{α} is the diffraction angle for the $K\alpha$ line.

θ_{β} is the diffraction angle for the $K\beta$ line.

A is the angle between the reciprocal lattice vector of the face plane of the crystal (121), and the reciprocal lattice vector of the plane from which the diffraction occurs.

$$R_{\alpha} = \mu_0 t_{\alpha} \epsilon$$

$$R_{\beta} = \mu_0 t_{\beta} \epsilon$$

$I_{0\alpha}$ is the intensity of the incident $K\alpha$ wavelength as defined before.

$I_{0\beta}$ is the intensity of the incident $K\beta$ wavelength.

$I_0(n_0)$, $I_0(n_0 \rho_0)$, $I_0(n_{\alpha})$, $I_0(n_{\alpha} \rho_{\alpha})$ are modified Bessel functions for specific arguments. All Bessel functions are zero order.

Dreiling and Dragsdorf⁵ showed that the integrated intensity of an x-ray diffracted beam is equal to, for a single polarization, $P = \cos 2\theta$

$$\rho_H = \frac{\pi}{2} \exp(-\mu_0 t) I_0(\mu_0 t \epsilon) \frac{C |F_H| |P|}{\sin 2\theta_{\alpha}}$$

For the case of two polarizations being present in the incident beam, the form for the integrated intensity is more complicated. There are now two terms, each of which contains a Bessel function of a different argument. The value of epsilon can be obtained by an iteration procedure. In the

equation,

$$(12) \quad I_H = \frac{\pi}{2} \exp(-\mu_0 t) \exp(-M) \frac{C |F_H|}{\sin 2\theta_0} \left[\beta_1 I_0(\nu_0 t \epsilon) + \cos 2\theta_0 \beta_2 I_0(\nu_0 t \epsilon + \cos 2\theta_0) \right]$$

f_1 and f_2 are the fractional parts of each polarization in the incident beam. For this experiment and unpolarized radiation $f_1 = f_2 = 1/2$. If the ratios of the integrated intensities of the $K\alpha$ and $K\beta$ line are considered, the following equation results:

$$\frac{\rho_{(K\alpha)\alpha}}{\rho_{(K\alpha)\beta}} = \left[\frac{I_{0\alpha}}{I_{0\beta}} \frac{\lambda_\alpha^2}{\lambda_\beta^2} \frac{\sin 2\theta_\beta}{\sin 2\theta_\alpha} \frac{\exp(-\mu_{0\alpha} t_\alpha)}{\exp(-\mu_{0\beta} t_\beta)} \frac{\exp(-M_\alpha)}{\exp(-M_\beta)} \right] \times \left[\frac{I_0(K_\alpha) + P_\alpha^2 I_0(P_\alpha K_\alpha)}{I_0(K_\beta) + P_\beta^2 I_0(P_\beta K_\beta)} \right]$$

All of the above parameters except ϵ are known. For the solution the equation was rewritten in the form

$$(13) \quad \frac{\rho_{(K\alpha)\alpha}}{\rho_{(K\alpha)\beta}} \left[\frac{I_{0\alpha}}{I_{0\beta}} \frac{\lambda_\alpha^2}{\lambda_\beta^2} \frac{\sin 2\theta_\beta}{\sin 2\theta_\alpha} \frac{\exp(-\mu_{0\alpha} t_\alpha)}{\exp(-\mu_{0\beta} t_\beta)} \frac{\exp(-M_\alpha)}{\exp(-M_\beta)} \right]^{-1} \left[I_0(K_\beta) + P_\beta^2 I_0(P_\beta K_\beta) \right] \\ = \left[I_0(K_\alpha) + P_\alpha^2 I_0(P_\alpha K_\alpha) \right]$$

This equation originally was solved graphically (see figure 16). A graph consisting of curves for both the left and right terms of the equation was drawn and the intersection gave the sought value for epsilon. However, the method was time consuming so a computer program was written to solve for epsilon.

In order to solve the equation by use of a computer, an iterative process is used in which a value of ϵ is picked between 0.0 and 1.0. If

EXPLANATION OF FIGURE 16

Graphical solution of equation for epsilon for 211 plane.

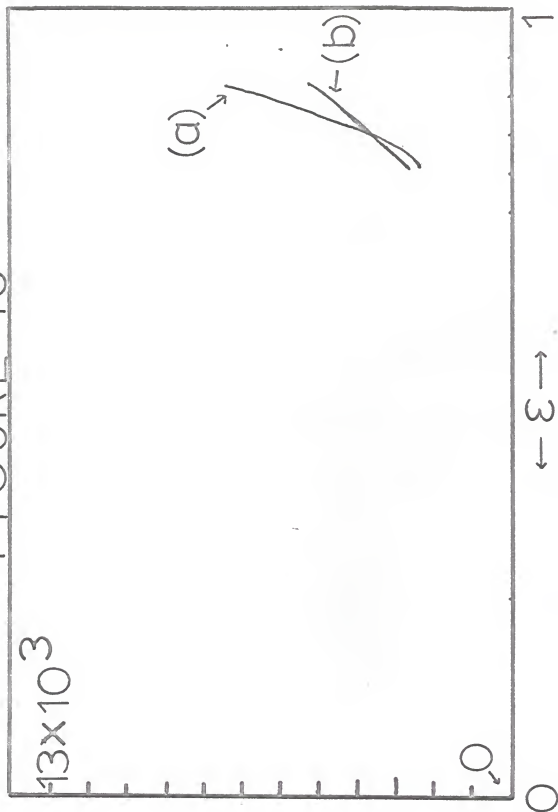
$$(a) \frac{f_{\text{ref}}}{f_{\text{ref}}(1)} \left[\frac{I_o}{I_{o2}} \frac{\lambda_o^2}{\lambda_o^2} \frac{\sin^2 \theta_o}{\sin^2 \theta_o} \frac{\exp(-K_o f_o)}{\exp(-K_o f_o)} \right]^{-1} \left[I_o(K_o) + P_o^2 I_o(P_o K_o) \right]$$

$$(b) [I_o(K_o) + P_o^2 I_o(P_o K_o)].$$

The value of epsilon is

approximately 0.85.

FIGURE 16



the left side of the equation is larger than the right side, the value of epsilon is increased by 0.1 and the terms are evaluated again. The process is repeated until the right side becomes larger than the left, at this time the value of epsilon is decreased by 0.01. This process is continued until a final value of epsilon, accurate to 0.001, is obtained. A listing of the program is in the appendix.

Table 4 shows the variation in the resulting value of ϵ as computer calculated for various assumed variations in the parameters of the equation relating the K_{α} to the K_{β} diffracted intensities. That is, equation 13 is rewritten here.

$$(14) \quad I_{\alpha}(h_{\alpha}) + P_{\alpha}^3 I_{\alpha}(P_{\alpha} R_{\alpha}) = K [I_{\alpha}(h_{\beta}) + P_{\beta}^3 I_{\alpha}(P_{\beta} R_{\beta})] \quad \text{where}$$

$$K = \frac{f_{\alpha}^0}{f_{\alpha}} \left[\frac{I_{0\alpha}}{I_{0\beta}} \frac{\lambda_{\alpha}^2}{\lambda_{\beta}^2} \frac{\sin 2\theta_{\beta}}{\sin 2\theta_{\alpha}} \exp(\mu_{0\beta} t_{\beta} - \mu_{0\alpha} t_{\alpha}) \exp(M_{\beta} - M_{\alpha}) \right]$$

has variables with potential errors. The table thus indicates directly the variation of ϵ for the fractional variation in the individual parameters.

The measurements of t_0 were taken five times with an average derivation of 0.0005 mm or 0.5 per cent. Two graphs each of the diffraction peaks were taken. In addition each peak was measured a minimum of three times. The largest percentage difference between any two measurements of the same line was 8 per cent for the (422) plane. For the other planes the percentage difference was less than 3 per cent. The values for μ_{α} and μ_{β} were taken from Cullity⁴ and may be considered accurate to 4 per cent.

TABLE 4
ERROR ANALYSIS

Parameter	Change in Parameter (Percentage)	Change in Epsilon (Percentage)
ρ_{hkl0}	5%	5%
$\rho_{hkl\alpha}$	5%	5%
t_*	5%	2.5%
μ_a and μ_s together	6%	2.8%

CONCLUSION

A comparison between the values of epsilon for the two theoretical and the experimental values of epsilon can now be made. The values for these three are presented in table 5.

TABLE 5

THEORETICAL AND EXPERIMENTAL VALUES OF EPSILON

Plane	Calculated Formal	Calculated H·r	Experimental
211	0.961	0.942	0.872
310	0.919	0.883	
422	0.919	0.883	0.662
10 $\bar{1}$	0.931	0.883	0.807
213	0.934	0.929	0.866
423	0.0194	0.108	

Several items are worthy of note. First, the experimental values for epsilon are all lower than the calculated values. The stronger diffracting planes are farther from agreement than the weaker diffracting planes (the 422 is an exception). This was not particularly startling, for exactly the same thing occurred in the measurements that Mwanje¹⁰ made on quartz. In table 6 the ratio of the experimental value of epsilon to the formal theoretical value is given for each plane.

TABLE 6

THE RATIO OF CALCULATED EXPERIMENTAL
VALUES OF EPSILON AND ROOT MEAN
SQUARE DISPLACEMENTS

Plane	ϵ_0/ϵ	$\langle u^2 \rangle^{1/2}$
211	1.10	0.37
h22	1.34	0.34
10 $\bar{1}$	1.16	0.36
213	1.07	0.20

Since the experimental and the calculated values of epsilon are related by the equation

$$\epsilon = \epsilon_0 \exp(-M) = \epsilon_0 \exp\left(-\frac{8\pi^2 \langle u^2 \rangle \sin^2 \theta}{\lambda^2}\right),$$

this ratio is simply a measure of the Debye Waller Factor \underline{M} . Since this factor is different for the different planes, herein lies an explanation for the low values of epsilon.

The two theoretical calculations should be different, because they represent two different ideas about the contribution of the various atoms to the total absorption of x-rays in the crystal. Actually the H-r method should give the highest values for epsilon, because it considers the atom as a point absorber. The formal theory considers the absorption by weighing each electron shell of each atom separately, and in doing so, produces lower values for epsilon. The fact that for this crystal this does not seem to hold, is due to a difference in the calculation for the total

absorption coefficient for the crystal. The H·r method yields a value of $\mu_0 = 205/\text{cm.}$ for copper K α radiation, whereas in the formal theory the value for μ_0 is $196/\text{cm.}$ If a common value for μ_0 is used for both calculations, then the H·r method will yield the higher values as predicted.

One other thing that could cause the experimental values for epsilon to be low is that the crystal may not have been absolutely perfect. It certainly did not yield as perfect a topograph as did the silicon crystals that Dreiling⁵ worked with nor as good as the quartz that Mwanje¹⁰ used.

That the value for epsilon is very dependent on crystal perfection is borne out by a set of similar experiments done on another crystal that had a noticeably imperfect topograph. The values for epsilon were almost 70 per cent lower than the calculated values.

It would seem, then, that the Lang method of determining crystal perfection is adequate to insure the establishment of the wave fields in the crystal.

SUMMARY

Anomalously large transmitted and diffracted x-ray beams have been observed as propagated through thick perfect crystals. These beams are anomalously large since the absorption does not follow the ordinary expression $I = I_0 \exp(-\mu_0 t)$, but more closely obeys an expression of the type $I = I_0 \exp[-\mu t(1 - \epsilon)]$ where epsilon, ϵ , is a parameter that is obtained from the Dynamical Theory of X-Ray Diffraction. Epsilon varies from zero to one depending on the particular type of crystal and from which plane in that crystal the diffraction takes place.

Vibration of atoms along a particular direction in the crystal is also related to the value of epsilon by the equation

$$\epsilon = \epsilon_0 \exp(-M) = \epsilon_0 \exp\left(-\frac{8\pi^2}{3} \langle u^2 \rangle \frac{\sin^2 \theta_0}{\lambda^2}\right)$$

where ϵ is the experimental and ϵ_0 is the theoretical value of epsilon. The mean square amplitude of lattice vibration is given by $\langle u^2 \rangle$, while θ_0 is the Bragg angle and λ is the wavelength of incident radiation.

Naturally occurring crystals of calcite were used for a determination of epsilon. Crystal structure perfection was determined by use of the Lang Topograph Technique. The crystals were polished in order to remove surface imperfections.

The experimental value of epsilon for a given plane was determined by using the ratio of the diffracted $K\alpha$ to the diffracted $K\beta$ integrated intensities. The $K\alpha$ and $K\beta$ integrated intensities were related by an equation involving a sum of two modified Bessel functions of zero order. A program was written to obtain an iterative solution to the Bessel equation. The values of epsilon for the 211, 422, 213, and 10 $\bar{1}$ planes obtained in

this manner were 0.872, 0.662, 0.866, and 0.807, respectively.

A comparison of the experimental values to the theoretical value of epsilon yielded the root mean square displacement of the atoms along the normals to the $10\bar{1}$, $h22$, 213 , and 211 planes. The values of $\langle u^2 \rangle^{1/2}$ obtained were 0.36, 0.34, 0.20, and 0.37, respectively.

REFERENCES

- (1) Batterman, Boris W.
Imaginary Part of X-Ray Scattering Factor for Germanium. Comparison of Theory and Experiment. J. Appl. Phys., 32:998-1001. 1961.
- (2) Batterman, Boris W., and Henderson Cole
Dynamical Diffraction of X-rays by Perfect Crystals. Rev. Mod. Phys., 36:681-717. 1964.
- (3) Borrmann, G.
Large Laue Diffracted Beam through Thick Quartz Crystals. Zeitschrift Fur Physik, 42:157. 1941.
- (4) Cullity, B. D.
Elements of X-Ray Diffraction. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts. 1959.
- (5) Dreiling, M.
Crystal Structure Information from Measurements of X-Ray Anomalous Transmission., A Ph. D. dissertation done under R. D. Dragsdorf at Kansas State University.
- (6) Hirsch, P. B.
The Reflexion and Transmission of X-Rays in perfect Absorbing Crystals., Acta Cryst., 5:176-181. 1952.
- (7) Honl, H.
Zur Dispersions Theorie Der Rontegenstrahlen., Zeitschr. F. Phys., 84:1. 1933.
- (8) Hunter, L. P.
Direct Measurements of the Angular Dependence of the Imaginary Part of the Atomic Scattering Factor of Germanium., IEM Journal, 106, April, 1959.
- (9) Lang, A. R.
Studies of Individual Dislocation in Crystals by X-Ray Diffraction Microradiography, Journal of American Physics, 30:11. 1959.
- (10) Mwanje, J.
Anomalous X-Ray Transmission by a Quartz Single Crystal., A master's degree thesis, Kansas State University.
- (11) Okkerse, B.
Temperature Effects in Anomalous Transmission., Phillips Res. Rept. 17, 464. 1964.
- (12) Parratt, L. G., and C. F. Hempstead
Anomalous Dispersion and Scattering of X-Rays., Phys. Rev., 94:1593-1600. 1954.

- (13) Wyckoff, R. W.
Crystal Structures, Interscience Publishers, Inc., New York. 1948.
- (14) Zachariasen, W. H.
 Theory of X-Ray Diffraction in Crystals, John Wiley and Sons,
 New York. 1945.
- (15) References which contain form factors for elements and ions:
- a. C, Keating, P., and Vineyard, G.
 Acta Cryst., 9:895. 1956
 - b. N, N⁻, O⁻, O⁺, O⁺², O⁺³, O, F, F⁻, Si⁺⁴, Si⁺³, Si, Ge
 Freeman, A. J.
 Acta Cryst., 12:929. 1959
 - c. Be, Na, Na⁺, Al⁺, Al⁺³, K⁺, Cl⁻, Ca, Ca⁺, Ca⁺³
 Freeman, A. J.
 Acta Cryst., 13:190. 1960
- (16) The samples of calcite used in this work were obtained from Dr. J. A. Bearden of Johns Hopkins University.

APPENDIX

COMPUTER PROGRAM FOR CALCULATION OF EPSILON

The following program was written and used for the calculation of epsilon from experimental data. An iterative process was used. An equation with epsilon dependent terms on both sides was solved by assuming an initial value of epsilon and incrementing this value until epsilon was found within 0.001.

On the data card the following values were read in

UA	The value of the linear absorption coefficient for $K\alpha$ radiation
UB	The value of the linear absorption coefficient for $K\beta$ radiation
TO	The thickness of the crystal measured with a micrometer caliper
WL	The ratio of the $K\alpha$ to $K\beta$ wavelengths
OBA	The ratio of the incident $K\beta$ to $K\alpha$ x-ray intensities
A	The angle between the normal to the surface (that the x-rays are incident upon) and the reciprocal lattice vector of the diffraction plane
OA2	Twice the Bragg angles in degrees for the $K\alpha$ and $K\beta$ wavelengths,
OB2	respectively
EA	The areas under the $K\alpha$ and $K\beta$ diffraction peaks, respectively
EB	
IPL	The numerical value of the reciprocal lattice vector for the diffraction plane
CRYST	The crystal identification
RAD	The type of target in the x-ray tube

PROGRAM TO COMPUTE EPSILON

```

RDD,RUN=FREE,TIME=10,PAGES=30,LINES=60,KP=29
00005 FORMAT(10(F7.3))
00010 FORMAT(10X,F9.6)
00015 FORMAT(' ', ' THE VALUE OF EPSILON OBTAINED FORM ANOMALOUS TRANSMI
*SSION OF X-RAYS FOR THE ',2A1,' PLANES OF ',4A1)
00017 FORMAT(' ', ' USING ',A2,' RADIATION IS ',F8.6)
DIMENSION IPL(2), CRYST(4), RAD(1)
00020 FORMAT(2A1,4A1,A2)
00025 FORMAT(10X,4(F15.6))
4001 FORMAT('1',18(A1))
401 FORMAT('0',4X,3(F15.6))
00035 FORMAT('0',2X,'UA',5X,'UB',5X,'TO',5X,'WL',5X,'OBA',5X,'A',5X,'OA'
*,5X,'OB',6X,'EA',5X,'EB')
400 FORMAT(18(A1))
AA=0.25
BB=AA/9.0
C=BB/16.0
D=C/25.0
E=D/36.0
FI=E/49.0
S=FI/64.0
T=S/81.0
U=T/100.0
V=U/121.0
WW=V/144.0
YY=WW/169.0
DIMENSION TITLE(18)
210 READ(1,400)TITLE
READ(1,5)UA,UB,TO,WL,OBA,A,OA2,OB2,EA,EB
READ(1,20)IPL,CRYST,RAD
OA=OA2/(2.0*57.295)
OB=OB2/(2.0*57.295)
A=A/57.295
TA=(TO/2.0)*(((1.0/SIN(OA+A))-(1.0/SIN(OA-A))))
TB=(TO/2.0)*(((1.0/SIN(OB+A))-(1.0/SIN(OB-A))))
UATA=UA*TA
UBTB=UB*TB
CA=COS(OA)
CB=COS(OB)
IF(UA)212,213,212
212 PA=2*CA**2-1.0
PB=2*CB**2-1.0
AP=UATA*PA
BP=UBTB*PB
ARU=(UATA-UBTB)
EXP=EXP(ARU)
CONST=(EA*OBA*WL*CA*EX)/(EB*CB)
BBB=SIN(OB+A)/SIN(A-OB)

```

PROGRAM TO COMPUTE EPSILON (continued)

```

BAA=SIN(OA+A)/SIN(A-OA)
CONST=CONST*(BBB/BAA)
HIO=0.0
EP=0.5
I=0
L=0
F=0.1
FF=0.01
FFF=0.001
OA=OA*2.0*57.295
OB=OB*2.0*57.295
WRITE(3,1001)TITLE
WRITE(3,35)
WRITE(3,5)UA,UB,TO,WL,OBA,A,OA,OB,EA,EB
DO 50 J=1,30
WRITE(3,10)EP
W=(UATA*EP)**2/1.0
X=(AP*EP)**2/1.0
Y=(UBTB*EP)**2/1.0
Z=(BP*EP)**2/1.0
CIO=1.0+W*(1.0+W*(AA+W*(BB+W*(C+W*(D+W*(E+W*(FI+W*(S+W*(T+W*(U+W*(
*V+W*(WW+W*YY))))))))))
DIO=PA(1.0+X*(1.0+X*(AA+X*(BB+X*(C+X*(D+X*(E+X*(FI+X*(S+X*(T+X*(U
*X*(V+X*(WW+X*YY))))))))))
EIO=1.0+Y*(1.0+Y*(AA+Y*(BB+Y*(C+Y*(D+Y*(E+Y*(FI+Y*(S+Y*(T+Y*(U+Y*(
*V+Y*(WW+Y*YY))))))))))
FIO=PB*(1.0+Z*(1.0+Z*(AA+Z*(BB+Z*(C+Z*(D+Z*(E+Z*(FI+Z*(S+Z*(T+Z*(U
**Z*(V+Z*(WW+Z*YY))))))))))
DIO=DIO*PA**2
FIO=FIO*PB**2
WRITE(3,25)CIO,DIO,EIO,FIO
CIO=CIO+DIO
EIO=CONST*(EIO+FIO)
GIO=CIO-EIO
WRITE(3,101)CIO,EIO,GIO
IF(L)190,58,190
00058 IF(I)70,60,70
60 IF(HIO)150,100,130
100 IF(GIO)120,200,110
110 EP=EP-F
HIO=GIO
GO TO 50
120 EP=EP+F
HIO=GIO
GO TO 50
130 IF(GIO)110,200,110
110 EP=EP+FF
I=1

```


PROGRAM TO COMPUTE EPSILON (continued)

```
HIO=GIO
GO TO 50
150 IF(GIO)120,200,160
160 EP=EP-FF
    I=1
    HIO=GIO
    GO TO 50
70 HR=GIO/HIO
    IF(HIO)170,200,180
170 IF(HR)175,200,140
175 EP=EP-FFF
    L=1
    HIO=GIO
    GO TO 50
180 IF(HR)185,200,160
185 EP=EP+FFF
    L=1
    HIO=GIO
    GO TO 50
190 HR=GIO/HIO
    IF(HIO)192,200,194
192 IF (HR)200,200,185
194 IF(HR)200,200,175
200 WRITE(3,10)EP
    WRITE(3,15)IPL,CRYST
    WRITE(3,17)RAD,EP
    GO TO 210
50 CONTINUE
    WRITE(3,10)EP
    WRITE(3,10)EP
    WRITE(3,15)IPL,CRYST
    WRITE(3,17)RAD,EP
    GO TO 210
213 STOP
    END
```

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Dr. R. Dean Dragsdorf for his guidance and encouragement throughout the program. Appreciation is also expressed to the Department of Education and the U. S. government for providing financial aid through a NDEA fellowship.

The author expresses appreciation to J. A. Bearden of Johns Hopkins University for providing the calcite crystals used in the experiment.

VITA

William Edward O'Connor was born March 5, 1944, in Fort Worth, Texas. He attended elementary school at Mount Carmel Academy in Fort Worth, Texas. He was graduated from Leneri High School in Fort Worth, Texas, in June, 1962. He entered St. Benedict's College in September, 1962. His B.S. degree in physics was granted in June, 1966, from St. Benedict's College, Atchinson, Kansas.

ANOMALOUS X-RAY DIFFRACTION THROUGH CALCITE

by

WILLIAM EDWARD O'CONNOR

B. S., St. Benedict's College, 1966

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1969

Anomalously large transmitted and diffracted x-ray beams have been observed as propagated through thick perfect crystals. These beams are anomalously large since the absorption does not follow the ordinary expression $I = I_0 \mu_0 t$, but more closely obeys an expression of the type $I = I_0 \mu_0 t(1 - \epsilon)$ where epsilon, ϵ , is a parameter that is obtained from the Dynamical Theory of X-Ray Diffraction. Epsilon varies from zero to one depending on the particular type of crystal and from which plane in that crystal the diffraction takes place.

Vibration of atoms along a particular direction in the crystal are also related to the value of epsilon by the equation

$$\epsilon = \epsilon_0 \exp(-M) = \epsilon_0 \exp\left(-\frac{8\pi^2}{3} \langle u^2 \rangle \frac{\sin^2 \theta_b}{\lambda^2}\right)$$

where ϵ is the experimental and ϵ_0 is the theoretical value of epsilon. The mean square amplitude of lattice vibration is given by $\langle u^2 \rangle$, while θ_b is the Bragg angle and λ is the wavelength of incident radiation.

Naturally occurring crystals of calcite were used for a determination of epsilon. Crystal structure perfection was determined by use of the Lang Topograph Technique. The crystals were polished in order to remove surface imperfections.

The experimental value of epsilon for a given plane was determined by using the ratio of the diffracted $K\alpha$ to the diffracted $K\beta$ integrated intensities. The $K\alpha$ and $K\beta$ integrated intensities were related by an equation involving a sum of two modified Bessel functions of zero order. A program was written to obtain an iterative solution to the Bessel equation. The values of epsilon for the 211, 422, 213, and 10 $\bar{1}$ planes were obtained in this manner. The values of epsilon obtained were 0.875, 0.687, 0.870 and 0.805.

A comparison of the experimental values to the theoretical value of epsilon yielded the root mean square displacement of the atoms along the normals to the $10\bar{1}$, $h22$, 213 , and 211 planes. The values of u obtained were $0.36, 0.34, 0.20$, and 0.37 .